Hindawi
International Journal of Chemical Engineering
Volume 2024, Article ID 9014776, 14 pages
https://doi.org/10.1155/2024/9014776

Research Article

Effective Removal of Ibuprofen from Aqueous Solution Using Cationic Surface-Active Agents in Dissolved Air-Flotation Process

G. Pooja,[1] **P. Senthil Kumar**,[2] **B. Chitra**,[1] **and Gayathri Rangasamy**[3,4]

[1]*Department of Chemical Engineering, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam 603110, India*
[2]*Centre for Pollution Control and Environmental Engineering, School of Engineering and Technology, Pondicherry University, Kalapet, Puducherry 605014, India*
[3]*Department of Civil Engineering, Faculty of Engineering, Karpagam Academy of Higher Education, Pollachi Main Road Eachanari Post, Coimbatore 641021, Tamil Nadu, India*
[4]*Department of Sustainable Engineering, Institute of Biotechnology, Saveetha School of Engineering, SIMATS, Chennai 602105, India*

Correspondence should be addressed to P. Senthil Kumar; senthilkumarp@pondiuni.ac.in

Received 14 January 2024; Revised 20 March 2024; Accepted 30 April 2024; Published 14 May 2024

Academic Editor: Giuseppe Pipitone

Copyright © 2024 G. Pooja et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

This research paper focuses on the removal of the nonsteroidal anti-inflammatory drug, ibuprofen, from an aqueous solution using a dissolved air flotation process. The comparison of different types of cationic surface-active agents such as cetyltrimethyl ammonium bromide (CTAB), tetrabutyl ammonium bromide (TBAB), and octyltrimethyl ammonium bromide (OTAB) have been employed to scrutinize the effective removal of the ecotoxic pharmaceutically active compound. The work included the influencing parameters such as pressure, contact time, surfactant dosage, pH, flow rate, and initial concentration owing to the best-optimized conditions. The maximum removal rate of 96.09% was achieved at 15 min for CTAB, TBAB had 62.36% at 45 min, and 89.6% was obtained for OTAB at 30 min, with 50 mg L^{-1} as the initial concentration and pH = 4. The removal rate was better with the optimized dosage of CTAB at 0.6 g, TBAB at 1.2 g, and OTAB at 1.0 g. It was observed that the geometric shape of the surface-active agents had greater impacts on the contaminants' efficiency. CTAB and OTAB were combined to find out the best possible removal rate of contaminants. The synergistic effect augments surfactant-based occurrence to be better in forming a good foaming effect and tends to have a lower critical micelle concentration (CMC). From the evaluation of kinetic models, pseudo-second-order flotation kinetics fitted the experimental data best. Furthermore, the formed metabolites that had been identified using gas chromatography-mass spectrometry were found to be less toxic than the parenting compounds.

1. Introduction

Toxic pollutants that are being emitted from domestic and industrial point sources without proper treatment are the major causes of wastewater pollution in urban areas. The requirement for water is increasing due to the variation in the environment, increase in population, and industrialization [1–5]. In the past few decades, the increase of newly identified compounds by anthropogenic or naturally occurring in surface water has turned into a global issue of escalating environmental concern. These compounds are termed organic contaminants popularly known as "emerging contaminants" (ECs) or "contaminants of emerging concern," found even in trace concentrations from parts per trillion to parts per billion and tend to bio accumulate over the period and pose a potential risk to flora and fauna. These contaminants include the chemicals found in pesticides, pharmaceuticals (drugs, natural and synthetic hormones), personal care products, fire retardants, plasticizers, food-added substances, and various other compounds released through household and industrial activities [6–11]. Amidst these toxic substances, more attention is paid to pharmaceutical and personal care products due to their tremendous creation and wide application. Intense concentrations of a few drug compounds, like ibuprofen (IBU) and sulfamethoxazole (SMX), have come to the

consideration of researchers concerning their effects on life in lakes, waterways, and groundwater. Unpredictable removal of unused prescriptions, terminated drugs, and veterinary meds is the major reason why they accumulate in water bodies such as streams, groundwater, surface water, soil, sludge, and sediment samples. IBU is one of the most popular and highly prescribed medicines in the world. It comes under the category of nonsteroidal anti-inflammatory drugs that have been used to relieve inflammation, fever, and pain involving rheumatoid arthritis, menstrual periods, and migraines [12–15]. This has been cataloged in the essential drugs list by the World Health Organization (WHO) in 2010. Though it varies from ng/L to μg/L, the maximum reported influent concentration was 60 mg/L. From the recent studies, it was deliberated that there is no limit set for this compound in the environment since it is an over-the-counter drug with more prescription volume and more excretion rate. Ibuprofen has a half-life period of 1.9–2.2 hours and is eliminated within 24 hours, so the piling of this compound in surface waters is more frequent. It is recognized in the range of moderate to higher concentration, and the recurrent discharge of these types of effluent without adequate treatment process could end up resulting in prolonged presence in the environment and may beget a negative impact on flora and fauna [16–20]. Thus, a treatment process is needed to figure out the successful cycles for eliminating these types of noxious pollutants from wastewater to accomplish the critical goal. There are many treatment processes available which entail membrane bioreactor, ultraviolet radiation, activated carbon, ozonation, conventional activated sludge, and wetland system, whereas due to their complex characteristics such as high capital cost, membrane fouling, a lot of chemical usage, and difficulty in operation, pharma compounds are not effectively removed [6, 21, 22]. Besides, flotation technology is an intriguing method to eradicate wastewater pollutants due to its ease of operation and low footprint.

Flotation technology is a unique physicochemical process that can treat different types of wastewaters likely electroplating, mechanical chemical polishing, textiles, fluoride-possessing wastewaters, papermaking, plastics segregation, and recycling. Various types of flotation processes are also enacted in water/wastewater treatment processes such as electroflotation, dissolved air flotation, sorptive flotation, dispersed air flotation, and adsorbing colloid flotation each of which holds distinct characteristics [23]. There are very few literature studies available on the treatment of nonsteroidal anti-inflammatory drugs (NSAIDs) and antibiotics using disparate flotation techniques. Some of them carried the removal of pharmaceutical contaminant in aqueous solution as well as real-time wastewater by utilizing a single type of synthetic-based surfactant [24–26]. The relationships between the parameters employed are still unclear in the references that are currently available, and the majority of them entail analysis using a certain kind of collector. So, the main reason for the current study is to scrutinize the best possible ways to remove ibuprofen from wastewater using the dissolved air flotation (DAF) process as this process brings in the separation of targeted contaminants through the generation of gas bubbles with the aid of surface-active agents. Concurrently, three types of cationic surface-active agents as cetyltrimethyl ammonium bromide (CTAB), n-octyl-trimethyl ammonium bromide (OTAB), and tetrabutylammonium bromide (TBAB) have been explored and compared to achieve better process effectiveness that was not carried out in other literature studies. Besides, integrated concept is gaining its importance in recent years such that the synergistic effect of best performing surface-active agents has been studied to discover the excellent recovery rates. Moreover, parameters such as initial concentration, surfactant dosage, pressure, pH, and retention time were evaluated in the study. The kinetics of flotation acting as a speculating tool was made to determine the relationship between contaminant concentration and time.

2. Materials and Methods

2.1. Chemicals and Materials. All the chemicals and reagents used were of analytical grade. Ibuprofen (IBU) (99% purity) with a molecular formula $C_{13}H_{18}O_2$ and n-octyl-trimethyl ammonium bromide (OTAB, $C_{11}H_{26}BrN$) extra pure, AR, 99% were procured from Tokyo Chemical Industry (India) Pvt. Ltd. The physicochemical characteristics of ibuprofen are shown in Table 1. Tetrabutylammonium bromide (TBAB, $C_{16}H_{36}BrN$) extra pure, AR, 99% and cetyltrimethyl ammonium bromide (CTAB, $C_{19}H_{42}BrN$) extra pure, AR, 99% were purchased from Sisco Research Laboratories Pvt. Ltd. The chemical characteristics of surface-active agents are summarized in Table 2. The stock solutions were prepared with distilled water. Operating solutions of IBU were produced by dissolving IBU ($100\,mg{\cdot}L^{-1}$) in distilled water which were subsequently dissolved to a desired concentration. The components required for the flotation unit were obtained from Dolphin Instruments and Equipments, Chennai.

2.2. Experimental Setup. The dissolved air flotation setup is a simple batch-type column as given in Figure 1. The setup consists of a flotation column attached to a compressor (voltage: 220–240 V) and an airflow meter (flow rate: 0-1 L/min) on the right side. Besides, the column was fabricated in acrylic material with a capacity of 850 ml, height of 25 cm, and 10 cm in diameter. The perforated column was designed to have 25 holes with an air bubble size of 50 μm fixed inside the column. A polyethylene tube with an inner diameter of 0.63 cm and an outer diameter of 0.95 cm was used for the column interconnection along with an air flow meter and a compressor. The airflow meter fabricated using polymethyl methacrylate (PMMA) comprises a control valve for managing the flow rate having a pressure of 0.1 Mpa.

2.3. Selection of Surface-Active Agents. One of the important factors to achieve successful flotation lies in the selection of surface-active agents. This is commonly called a "surfactant," as it decreases the surface tension, thus boosting its wetting

Table 1: The physicochemical properties of ibuprofen.

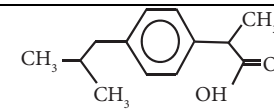
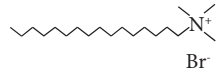
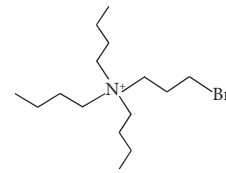
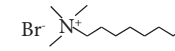
Formula	$C_{13}H_{18}O_2$
Solubility (mg/L)	21.0
Structure	
Molecular weight (g/mol)	206.29
pKa	4.91

Table 2: The chemical properties of the surface-active agents used for IBU removal.

Properties	CTAB	TBAB	OTAB
Structure			
Formula	$C_{19}H_{42}BrN$	$C_{16}H_{36}BrN$	$C_{11}H_{26}BrN$
MW (g/mol)	364.45	322.37	252.23

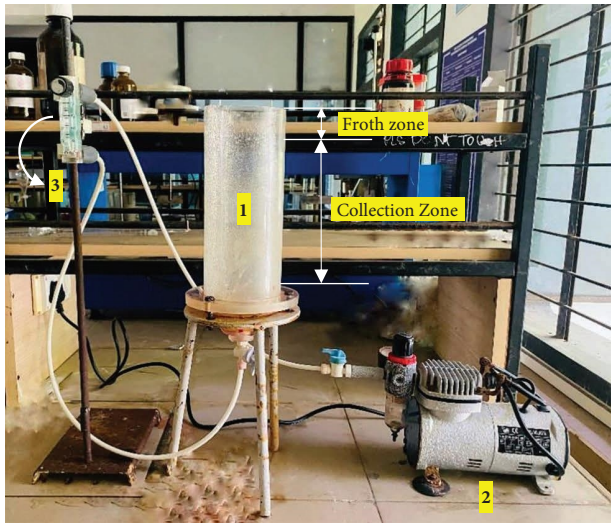


Figure 1: An experimental air flotation set-up in a laboratory: (1) flotation column, (2) compressor, and (3) air-flow meter.

and spreading properties. Based on the categories of non-ionic, cationic, and anionic that exist on the market, there are numerous types of surfactants. One such type used in this work is cationic-based. Like other surfactants, it has polar and nonpolar groups possessing a quaternary ammonium unit and various alkyl groups, respectively. They carry positively charged ions on their hydrophilic head and can firmly adsorb on the contaminants with negatively charged groups via charge-charge or electrostatic interactions. The chosen surface-active agents in this experiment work better by providing good solubility and foamability when compared with other types, thereby increasing the flotation efficiency better by decreasing CMC formation [27–32]. Figure 2 explains the mechanism model of the surface-active agents that tend to be connected with contaminants.

2.4. Flotation Procedure. The dissolved air flotation is a process that targets the concentrated contaminant based on the variations in physicochemical properties. Each batch of the solution's initial volume (Vo) was prepared in a 500 ml volumetric flask. As IBU is not water-soluble, a very small quantity of ethanol was used to dissolve IBU and made up to the intended volume with distilled water. Initially, the prepared stock solution was first fed into the flotation column followed by conditioning for 1 minute [33–35]. Surface-active agents were added gradually at various dosages for solutions containing different concentrations. They provide proper greater adhesion of particles to bubbles and ions, thus promoting effective transfer to the solution's surface. When fluid phases with varying degrees of polarity and hydrogen bonding, such as air/water interfaces, are in contact with one another, the hydrophobic and hydrophilic moieties get partitioned out. Microbubbles are formed when the air is dissolved at greater pressure in the saturator when the solution present in the flotation column is liberated with atmospheric pressure. Thus, they produce an amicable environment to the froth to be strong enough to protect against scum ruination.

Typically, the high-efficiency rate of flotation depends on the size of the bubbles as well as the chosen surface-active agents [36–38]. Bubbles with a size above 150 μm tend to have bubble clusters resulting in poor removal. Hence, in this work, the midsized bubbles (50 μm) are employed as they can provide better lifting power. After achieving a significant amount of retention time, the clear liquid is gathered at the bottom, while the froth is ejected at the top. All the experiments were carried out in triplicate. Furthermore, for every flotation experiment, a fresh batch of

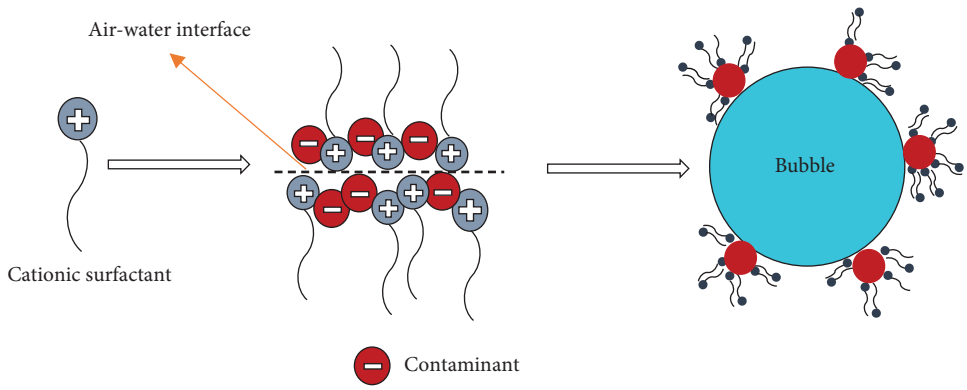


Figure 2: Micelle aggregation of the cationic surfactant with a hydrophobic particle.

stock solutions needs to be prepared. The stock solution flasks were properly cleaned before preparation and externally wrapped with aluminum foil to avoid photodegradation.

2.5. Analysis

2.5.1. UV-Visible Spectroscopy Analysis. Ibuprofen was quantified using a UV-670, UV-VIS spectrophotometer from Jasco. Through the visual inspection of the spectrum, the absorption maxima were observed at wavelength (λmax) 222 nm [39]. The supernatant obtained after each run of the flotation was enacted for the quantitative analysis using UV-VIS. As the pharmaceutical compounds are light sensitive, the collected samples for analysis were wrapped with the aluminium foil as well and the analysis was carried out immediately after each trial to avoid degradation. At the end of each trial session, utilised laboratory glassware and the flotation column were consistently rinsed with distilled water in order to enhance better results.

2.5.2. GC-MS Assay. Through GC-MS, qualitative analysis was made to find out the metabolites if any formed during the process. The Clarus 680 GC was used in the analysis of pharmaceutical compound degradation with a fused silica column, packed with Elite-5MS (5% biphenyl 95% dimethylpolysiloxane, 30 m × 0.25 mm ID × 250 μm df), and the elements were separated using helium as a carrier gas with a constant flow of 1 ml/min. The injector temperature was set at 260°C during the chromatographic run. The 1 μL of extract sample was injected into the instrument accompanying the oven temperature as follows: 60°C (2 min); followed by 300°C at the rate of 10°C min^{-1}; and 300°C, where it was held for 6 min. The total run time was up to 30 minutes.

2.5.3. Dynamic Surface Tension Measurements. The surface tension was measured using a DY-300, Kyowa Interface Science Co., Ltd using a movable plate method at a temperature of 27°C. The platinum plate and glass containers were thoroughly washed with deionized water. Before carrying each experiment, the plate was flame dried. Surface tension was taken to be at equilibrium, when the average standard deviations of the five consecutive values did not exceed 0.10 mN/m.

3. Results and Discussion

3.1. Effect of Surface-Active Agents. Aforementioned, this is one of the paramount operating parameters for successful flotation. Figure 3 shows variations in IBU removal using different surface-active agents keeping other parameters constant. The dosages that were varied to attain better removal lie from 0.2 g to 1.4 g. The maximum removal efficiency concerning CTAB was about 96.09%, TBAB had 62.36%, and 89.6% was for OTAB. When compared with the three surface-active agents, a better removal rate was observed at 0.6 g of CTAB as it possesses 16 carbons, whereas the target contaminant has 13 carbons. So, the better removal efficiency was achieved in 15 min which denotes that the IBU had the highest affinity to produce micelles with CTAB.

Besides, IBU removal was good with the other two surfactants on the dosages of 1.0 g and 1.2 g for OTAB and TBAB, respectively. Since TBAB has lesser foaming ability compared with CTAB, lesser dosages do not yield the expected results. The performance of OTAB with IBU was fair enough as OTAB has 8 carbons. In addition to that, the results with TBAB were very poor as it is a branched alkyl chain compound, but the other two surface-active agents were linear alkyl chain compounds. It can be inferred that the geometric shape of the surfactants tends to be one of the deciding factors to procure a better removal rate [40]. The variations of dynamic surface tension with three surfactants at different dosages in flotation are shown in Figure 4. The same behaviour was observed for all the surfactants that the surface tension got reduced with the increase in the surfactant dosage, and this may be due to the fact that the adsorption of surfactant monomers at the air-water interface and tension remains constant after attaining the critical micelle concentration. The surface tension of double distilled water was about 71.85 mN/m. It was found that the value of surface tension for CTAB decreased to 28.52 mN/m which showed the greatest affinity, TBAB of 47.2 mN/m, and OTAB of about 31.06 mN/m.

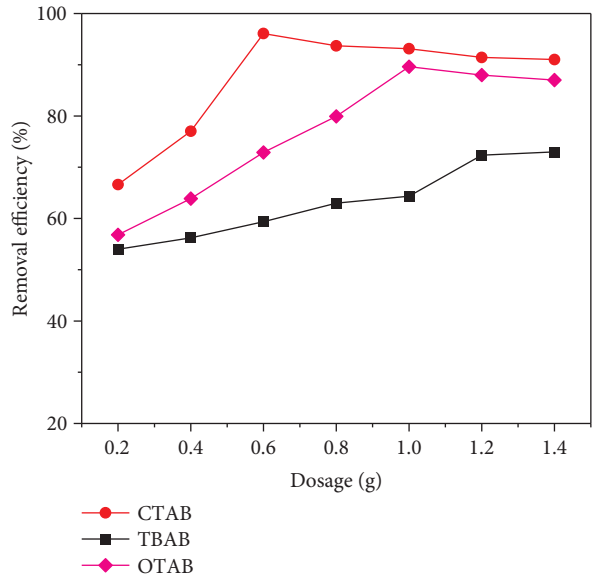


Figure 3: Changes in separation rates over surfactant dosage (pH 4.0, (CTAB) = 20 psig, 15 min; (OTAB) = 25 psig, 30 min; (TBAB) = 25 psig, 45 min).

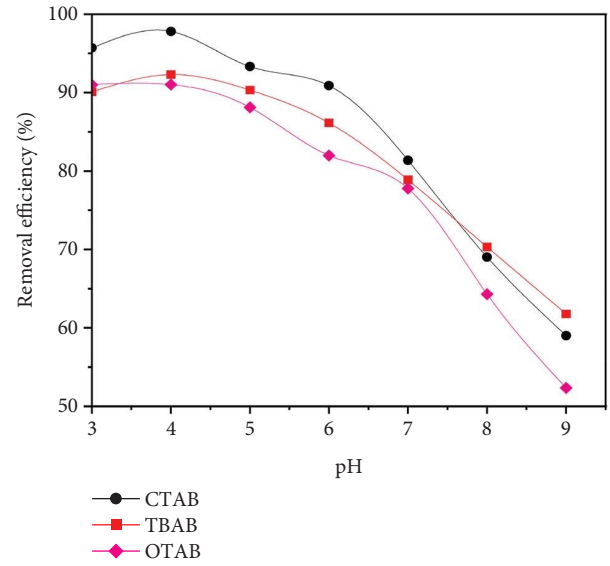


Figure 5: Changes in separation rates over pH (CTAB = 20 psig, 15 min, 0.6 g; OTAB = 25 psig, 30 min, 1.0 g; TBAB = 25 psig, 45 min, 1.2 g).

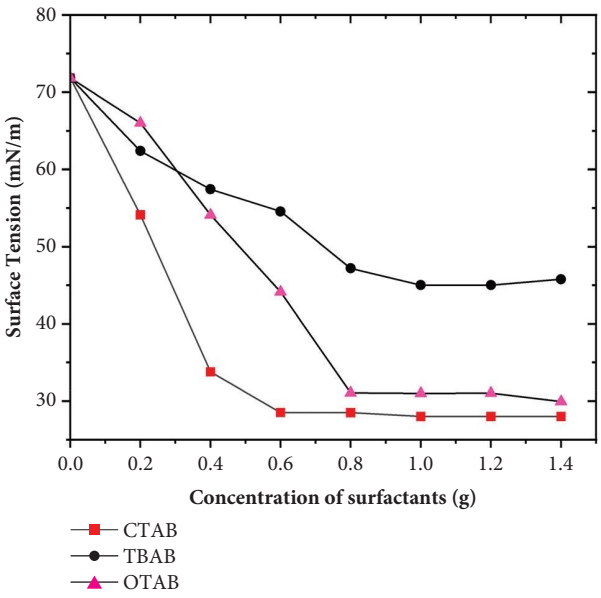


Figure 4: Effect of cationic surfactants concentration on the surface tension (pH 4.0, (CTAB) = 20 psig, 15 min; (OTAB) = 25 psig, 30 min; (TBAB) = 25 psig, 45 min).

3.2. Effect of pH and Concentration. It is crucial to comprehend the impact of pH on the removal process since changes in solution pH affect the IBU speciation. Ibuprofen has a pKa value of 5.2, and they occur in neutral form at pH < pKa. This compound occurs as neutral species at coexists at neutral and anionic at pH≈pKa and occurs as anion species at pH > pKa. Ibuprofen appears in neutral form at pH 4 which is below pKa and in anionic form above pKa at pH 7. Figure 5 shows the effect of pH on the removal efficiency of IBU by flotation. The experiment was validated at pH 4 (acidic), around pKa of pH 5.3, and pH 7 (neutral) to scrutinize the sorption of ibuprofen with anionic, neutral, and neutral/anionic species onto the sediment [41]. Ibuprofen is a weak acid, and its removal was favorable at pH 4 and unfavourable at pH 7. Acidic pharma compounds are neutral molecules, that is, the pH which is below pKa, interacting with the column surface via nonelectrostatic interaction by entailing hydrogen bonds. In this experiment, at pH 4 (lesser than pKa), ibuprofen neutral was sorbed via nonelectrostatic interaction with the settling surface and this follows [42]. The rate of removal decreases with the increase in pH as there occurs deprotonation of surface-active agents which made it very complex to act on ibuprofen, obstructing the formation of agglomerates [43–45].

The concentration of IBU was varied from 25 mg L^{-1} to 100 mg L^{-1}. The separation efficiency concerning the initial concentration is shown in Figure 6. As the concentration increases, the separation rate decreases. Stable froths were formed when increasing the concentration from 25 mg L^{-1} to 50 mg L^{-1}. The maximum removal rate of about 96.51% was observed at 50 mg L^{-1} with CTAB, 74.11% for OTAB, and 64.44% for TBAB. The rate of particle-air bubble collision and detaining probability lead the way to the production of charged froths at 50 mg L^{-1}, balanced by fine particles. Moreover, there was a sufficient contact between the contaminant and surface-active pairing. The TBAB results were not as expected since it possesses a shorter chain length and exhibited lesser binding efficiency. Besides, attaining the critical point, the rate of removal decreases at 75 mg L^{-1} and 100 mg L^{-1} for CTAB and OTAB. This is due to the following factors: (1) formation of complexes with other ions, (2) attachment site competition, (3) saturation of air bubbles, and (4) the size of the bubbles getting reduced [46, 47].

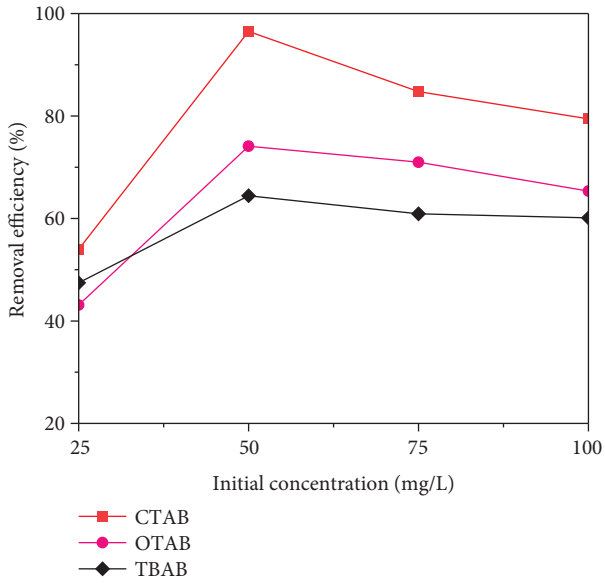


Figure 6: Changes in separation rates over initial concentration (pH 4.0, (CTAB) = 15 min, 0.6 g; (OTAB) = 30 min, 1.0 g; (TBAB) = 45 min, 1.2 g).

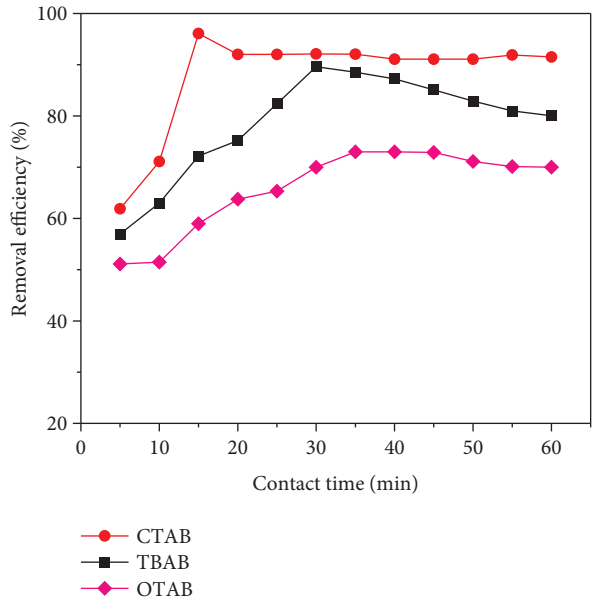


Figure 7: Changes in separation rates over contact time (pH 4.0, (CTAB) = 20 psig, 0.6 g; (OTAB) = 25 psig, 1.0 g; (TBAB) = 25 psig, 1.2 g).

3.3. Effect of Contact Time. The effect of contact time concerning the flotation removal rate has been discussed after finding out the system composition. The flotation time was varied from 5 to 60 min, and the samples were taken at every 5 min, which is shown in Figure 7. As mentioned, the removal efficiency of the contaminant with CTAB of about 96.09% was achieved in 15 min. The removal rates with OTAB and TBAB were obtained at 30 min and 45 min, respectively. Certainly, the flotation mechanism involves three phases: (1) true flotation, that is, the particle-bubble attachment, (2) entrainment, and (3) drain. The first two processes appear in the suspension zone, while the last one takes place in the froth zone. In the froth zone, liquid film thinning happens due to free water gravitational drain, by which the interfacial tension influences the firmness of liquid film between the solid-liquid interface [48–50]. From the procured results, it can be seen that the rate of removal escalates with the increase in flotation time. It was observed that, for CTAB, there was a rapid removal within 15 minutes. This is because the ideal flotation time made the target contaminant thoroughly contact with the formed micelles, and there occurred a high chance of particle bubbles colliding (target object and bubbles) and bubble surface loading increased [40]. However, the prolonged flotation time made the interface between the two phases impaired, and this applies to every surface-active agent.

3.4. Effect of Flow Rate and Pressure. The flotation rates were determined as a function of flow rates that were varied from 0.25 L/min to 1.0 L/min by keeping other parameters constant. It was observed that the bubble agglomeration could not be seen on the flow rate of 0.25 L/min. The flotation recovery rates increased to the maximum and decreased with the increase in the flow rate at 0.75 and 1 L/min, and it was due to the formation of bubble coalescence [51]. So, the optimized flow rate was found at 0.5 L/min which is shown in Figure 8.

The flotation study was conducted with a pressure variation from 5 psig to 30 psig (pound per square inch), and pressure was varied for every 5 psig. The size of the bubbles is affected due to the differences in the pressure given across the system. It was reported that the bubble size that is produced below the pressure of 4–6 atmospheres is generally reported to be in the size between 10 and 100 μm keeping the average size of 40 μm [52]. Accordingly, the chosen bubble size in this experiment is 50 μm. From the procured results, the maximum removal was perceived at 20 psig with CTAB and 25 psig for OTAB and TBAB. It was apparent that the removal efficiency escalates with the increase in pressure which implies that it can bear a greater number of contaminants to the air-water interface and improves the removal rate of IBU [53]. However, it was identified that there is a critical point, after which the removal rate decreases as seen in Figure 9, exhibiting the removal rate of IBU concerning pressure. After 20 psig, the rate of removal declines due to bubble coalescence ensuing in the dissemination of some of the contaminant-collector precipitates that get back into the bulk solution. As a consequence, there is an inadequate contact between the surface-active agent and the contaminant [54].

3.5. Synergistic Effect of Surface-Active Agents. CTAB and OTAB were combined to find out the best possible removal rate of contaminants and the synergistic effect of surfactants. It was observed that the cationic/anionic (IBU) systems indicated improved synergism and formation of mixed micelle. It was observed that there was a complete removal by flotation in 25 min with 0.4 g and a pressure of 20 psig.

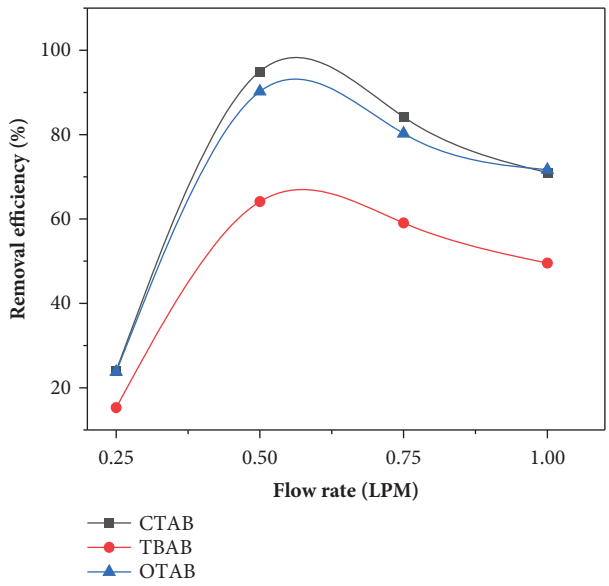


Figure 8: Changes in separation rates over flow rate (pH 4.0, (CTAB) = 20 psig, 0.6 g; (OTAB) = 25 psig, 1.0 g; (TBAB) = 25 psig, 1.2 g).

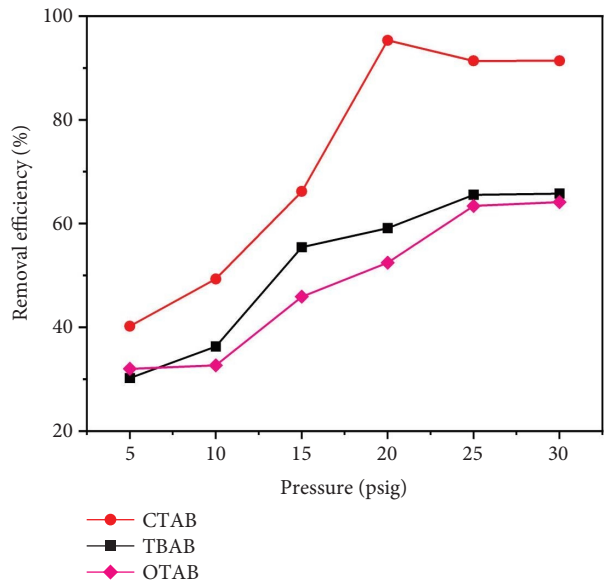


Figure 9: Changes in separation rates over pressure (pH 4.0, (CTAB) = 15 min, 0.6 g; (OTAB) = 30 min, 1.0 g; (TBAB) = 45 min, 1.2 g).

This synergistic effect augments surfactant-based occurrence to be better in forming a good foaming effect and tends to have lower CMC. As both of them are linear alkyl chain compounds, the surface-activeness was more than the application of individual surfactants [55–59]. The elimination of contaminants was marginal at higher dosages of the combined surfactants, such that the optimal dosages must be employed. The removal percentage of ibuprofen with the integrated surface-active agents is shown in Figures 10 and 11.

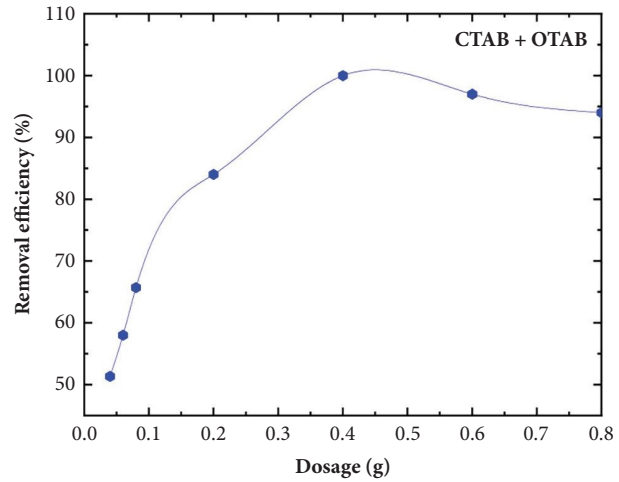


Figure 10: Changes in separation rates over integrated surfactant dosage (CTAB + OTAB = 20 psig).

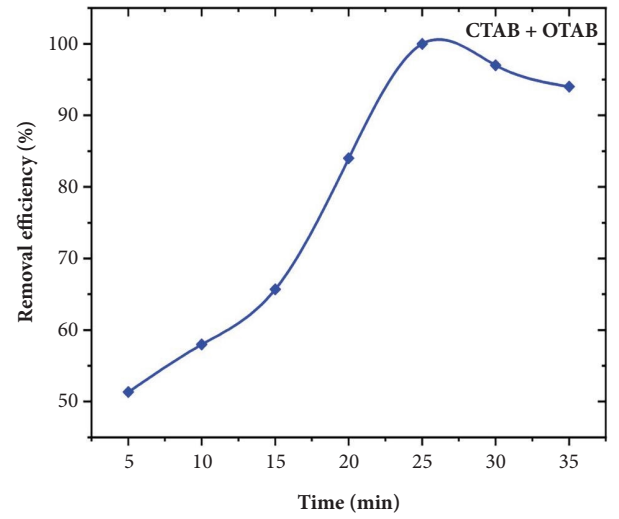


Figure 11: Changes in separation rates over integrated surfactant dosage (CTAB + OTAB = 20 psig; dosage = 0.4 g).

3.6. Gas Chromatography Mass-Spectrometry Analysis (GC-MS). As flotation involves phase change but to identify the metabolites formed and understand its level of toxicity, GC-MS analysis was performed. Full scan mass spectra of Ibuprofen in Figure 12 were taken as a precursor which had a m/z of 205.11 with the retention time of 4 min. Analytical GC/MS outcomes of solutions after the interaction between ibuprofen and the surface-active agents in Figure 13 show the relative intensity of formed metabolites in the supernatant. A very few literature studies were available on the analysis of GC-MS of pharmaceutical compounds with respect to cationic surfactants. From the observed chromatographic profile for ibuprofen in accordance with TBAB, the existence of TBAB was confirmed by its mass spectrum through the fragments formed of long-chain aldehydes such as tri-decanal (with high intensity), DL-3-amino butyric acid, and N-hexadecenoic acid at a retention time of 1.62, 2.68, and 15.96, respectively. The contaminant peak

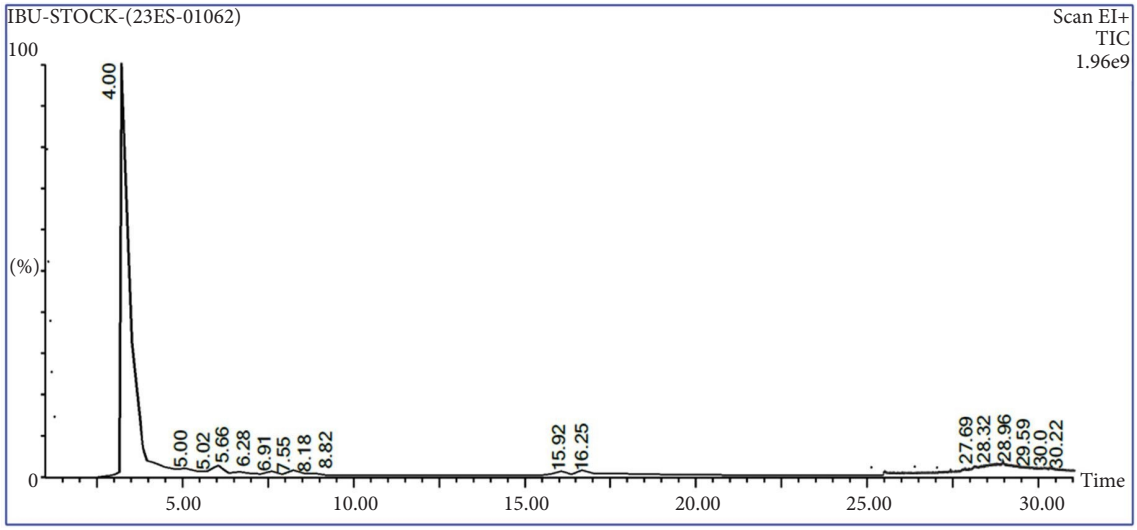
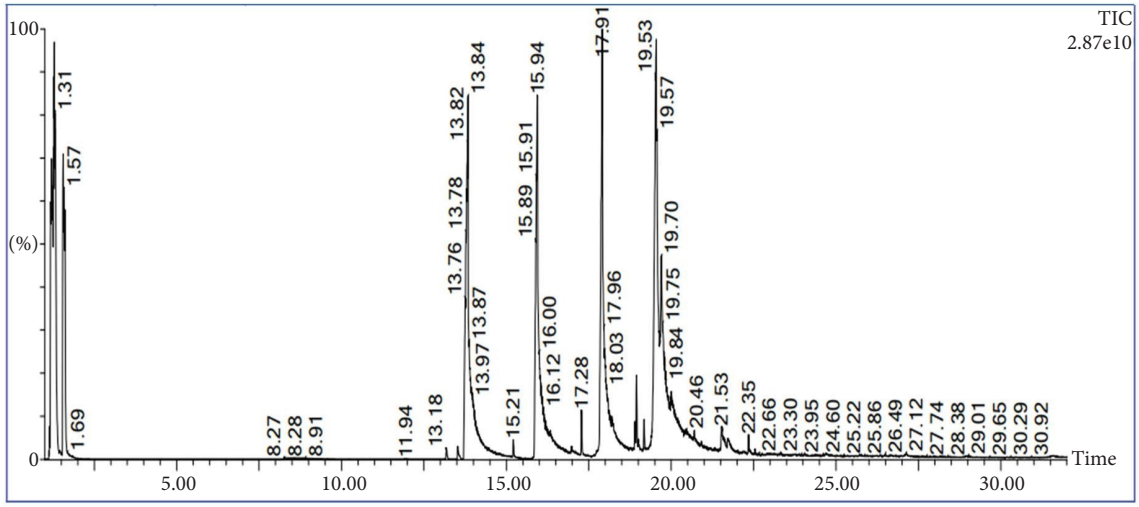
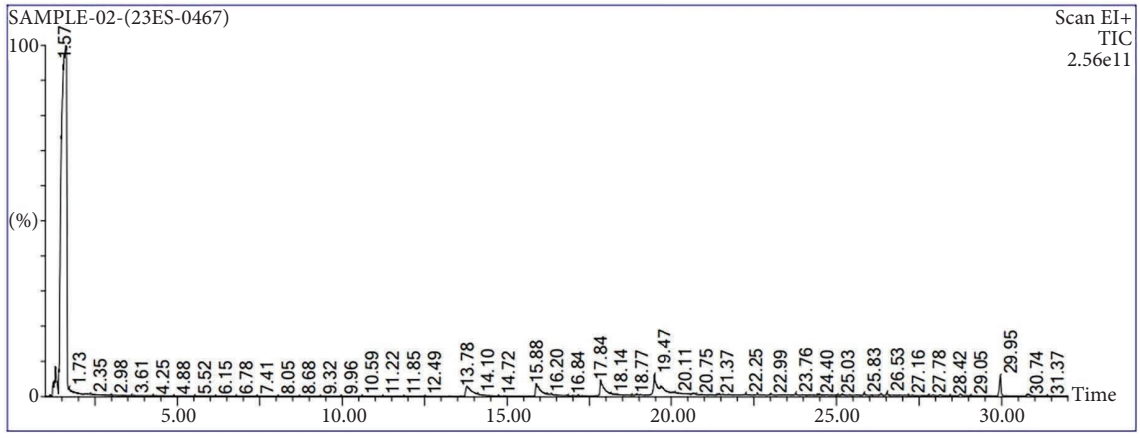


Figure 12: Chromatogram on the full scan of ibuprofen precursor.

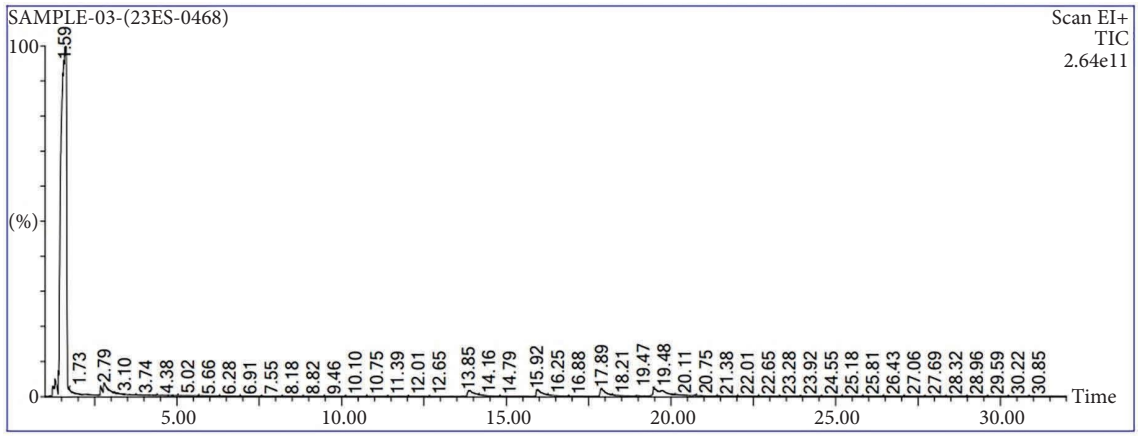


(a)



(b)

Figure 13: Continued.



(c)

Figure 13: Chromatogram on the removal of contaminant using different surface-active agents (a) Ibu + CTAB (b) Ibu + OTAB (c) Ibu + TBAB.

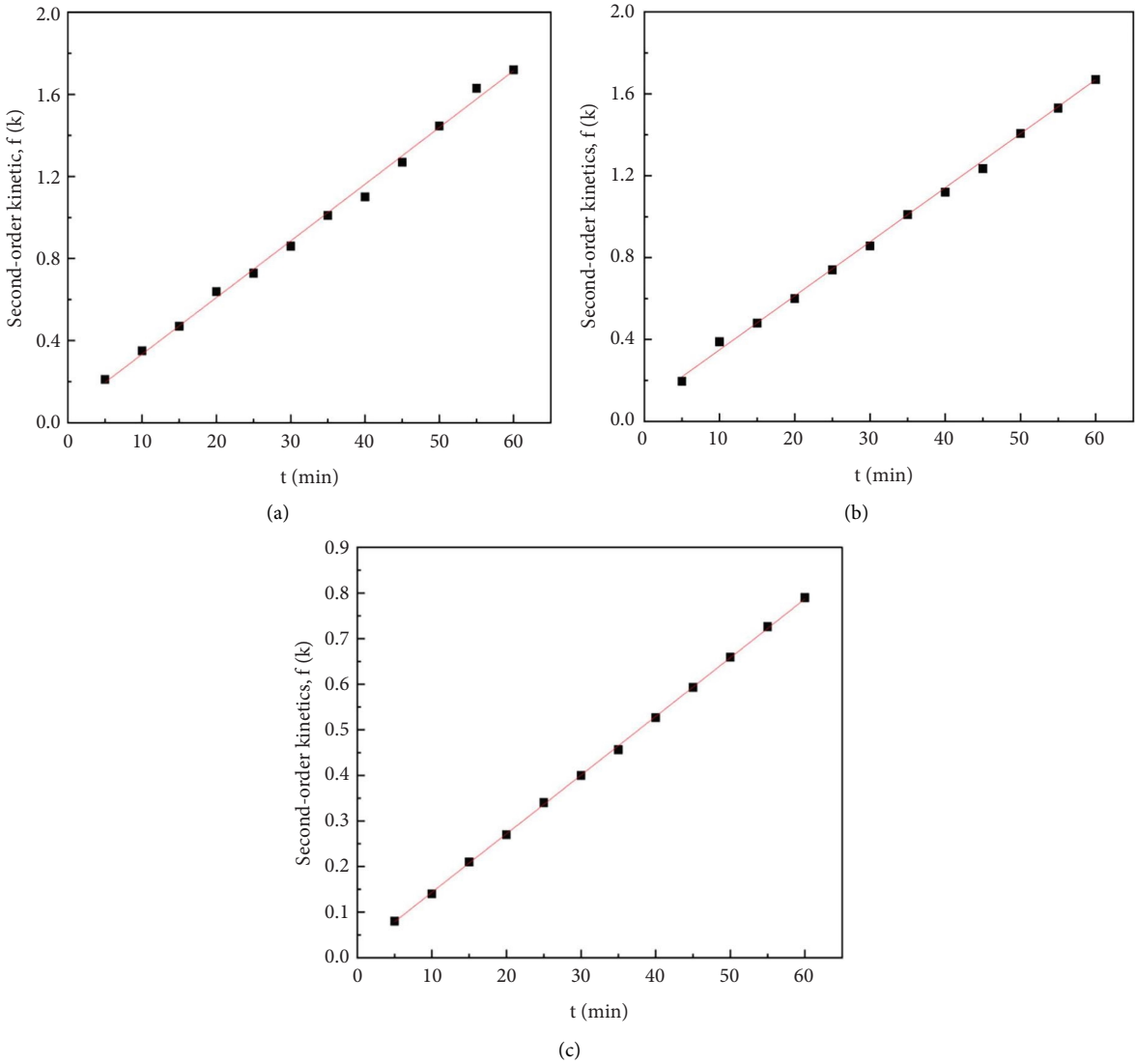


Figure 14: Pseudo-second-order flotation kinetics plots for (a) tetrabutyl ammonium bromide (TBAB), (b) octyltrimethyl ammonium bromide (OTAB), and (c) cetyltrimethyl ammonium bromide (CTAB).

Table 3: Comparison of pseudo-first and second-order kinetic parameters for pharma compound under various surface-active agents.

	Pseudo-first order		Pseudo-second order	
	k_1	R^2	k_s	R^2
TBAB C_0 (mg/L)				
25	0.00031	0.5551	0.018	0.9909
50	0.00029	0.7812	0.013	0.9912
75	0.00025	0.6942	0.011	0.9912
100	0.00021	0.6161	0.014	0.9913
OTAB C_0 (mg/L)				
25	0.00021	0.6444	0.006	0.9933
50	0.00029	0.7876	0.008	0.9949
75	0.00028	0.7361	0.007	0.9944
100	0.00014	0.6103	0.003	0.9939
CTAB C_0 (mg/L)				
25	0.00025	0.6951	0.010	0.9959
50	0.00024	0.9816	0.019	0.9966
75	0.00029	0.7469	0.011	0.9966
100	0.00029	0.6750	0.012	0.9961

derivatives were not visible as they occurred in a trace amount and the formed intermediates due to surface-active agents were high [60–63].

In the case of OTAB, a high intensity of 2-octanol, 2,6-dimethyl was visible with a retention time of 1.6 minutes. Also, eicosanoic acid with a retention time of 17.83 and oleic acid with 19.67 minutes were observed. The formed compounds were a residue of ibuprofen degradation during the process. In this sense, there occurred complete degradation of the pharma compound, while some derivatives were found during the interaction of IBU with a CTAB, a surface-active agent. The formed derivatives were 14-pentadecanoic acid with high intensity, tetra decanoic acid, dodecanoic acid, and methyl 9-eicosenoate [64, 65]. All tested derivatives possessing high intensity are less toxic than the parenting compounds.

4. Flotation Kinetics

Flotation kinetics, which is paramount in illuminating the mechanism of the process and acting as predictive tools in the use of flotation technology, is employed to scrutinize the variation of concentration over time. The present work investigates the flotation rate in accordance with the most extensively used pseudo-first order (1)and second order kinetics (2) Also, concerning the different surface-active agents employed in the research, the flotation kinetic models have also been employed to CTAB, OTAB, and TBAB to predict the best possible removal mechanism. The following equations illustrate the kinetic models as

$$R = R\infty \cdot 1\left(1 - e^{-k_1 t}\right). \quad (1)$$

For assessing flotation performance, the flotation rate constant (K) and maximum theoretical recovery ($R\infty$) are the helpful indicators, while t represents the flotation time [66, 67].

$$R = \frac{R_{\infty,5}^2 K_5 t}{1 + R_{\infty,5} K_5 t}. \quad (2)$$

The graphs are allotted, and the R^2 values are taken. The degree of accuracy of linear fit was quantified by a higher R^2 value. Even the retention time of flotation is extended indefinitely, and it is unlikely that the recovery of hard floating particles with weak hydrophobicity will be 100%. Figure 14 shows the plots of experimental data fitted by the two kinetic models occurred at different flotation time intervals, pertaining to the actual flotation yields [54, 68–70]. The parameters of the kinetic models are summarized in Table 3.

In comparing with the pseudo-first order kinetic model, the flotation kinetics of surface-active agents with respect to the contaminant could be well described by pseudo-second order kinetics. In accordance with the variance between the estimated and the experimental outcomes, holds the R^2 value of CTAB, OTAB, and TBAB as 0.9966, 0.9949, and 0.9912, respectively, which follows [71]. Therefore, it may be said that the pseudo-second-order kinetic model suits well to describe the flotation behaviour of the contaminant eradication.

5. Conclusion

The study focused on the removal of an emerging contaminant from an aqueous solution using flotation technology. A full-pressurised dissolved air flotation process was employed, as an environmentally friendly and sustainable approach. The different experimental conditions have been carried out with the optimization of influencing parameters such as surfactant dosage, pH, retention time, pressure, flow rate, and initial concentration. From the analysis obtained and discussions that were presented in the preceding sections, concluding remarks may be drawn as follows: this technology is well known for its minimal generation of sludge and high throughput despite its difficulty in removing scum [47, 72].

Comparison of various cationic surface-active agents such as cetyl trimethyl ammonium bromide (CTAB), tetrabutyl ammonium bromide (TBAB), and octyltrimethyl ammonium bromide (OTAB) has been employed.

The scrutinization of the study was made to profoundly understand the behaviour, acclimatization, and drawbacks of those collectors on the effective removal of the pharmaceutical compound.

(1) Among the three surface-active agents used, it was observed that the CTAB contributed effectively to the removal of ibuprofen through dissolved air flotation. The rate of removal of about 96.09% was achieved at 15 min for CTAB, while TBAB had 62.36% at 45 min, and 89.6% was obtained for OTAB at 30 min.

(2) Moreover, the structures of the cationic collectors possess a greater impact on the removal of the contaminant. It can be inferred that the performance of the branched alkyl chain compound, TBAB, was very poor. However, the other two cationic collectors with a similar structure in the alkyl chain are found to be the ideal collectors for the flotation process providing good foamability. CTAB and OTAB were combined to find out the best possible removal rate of contaminants. The synergistic effect augments surfactant-based occurrence to be better in forming a good foaming effect and tends to have lower critical micelle concentration (CMC).

(3) On the other hand, the formed metabolites that had been identified using gas chromatography-mass spectrometry are found to be less toxic than the parenting compounds. The effect of cationic collectors' performance of ibuprofen was also studied from the perspective of flotation kinetic models. Nevertheless, two kinetic models have been made, and we found that the pseudo-second-order kinetic model possesses a greater fitting accuracy ($R^2 > 0.998$), and the fitted curve more precisely depicted how the concentrate yield differed over time. As an outcome, it can be concluded that the pseudo-second-order kinetic model is more suited to represent the contaminant's floating behaviour.

(4) Furthermore, the dissolved air flotation process possesses advantages of being efficient and simple, having the ability to remove all types of pollutants, having less retention time, and causes the generation of sludge. But the main disadvantage of the process lies in the difficulty of removing scum, which requires a necessary attention. Additionally, given the experimental conditions tested, the collector used in this process produces improved separation efficiency and might be successfully applied [73].

Abbreviations

EC: Emerging contaminant
IBU: Ibuprofen
NSAID: Nonsteroidal anti-inflammatory drug
DAF: Dissolved air flotation
CTAB: Cetyltrimethyl ammonium bromide
TBAB: Tetrabutyl ammonium bromide
OTAB: Octyltrimethyl ammonium bromide
CMC: Critical micelle concentration
UV-VIS: UV-visible spectrophotometer
GC-MS: Gas chromatography-mass spectrometry.

Data Availability

Data will be made available on request to the corresponding author.

Ethical Approval

This article does not contain any studies involving animal or human participants performed by any of the authors.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

G. Pooja performed investigation, methodology, and writing of the original draft. P. Senthil Kumar performed conceptualization, validation, and supervision. B. Chitra and Gayathri Rangasamy conducted data curation, formal analysis, and visualization.

References

[1] H. Karimi-Maleh, M. Shafieizadeh, M. A. Taher et al., "The role of magnetite/graphene oxide nano-composite as a high-efficiency adsorbent for removal of phenazopyridine residues from water samples, an experimental/theoretical investigation," *Journal of Molecular Liquids*, vol. 298, 2020.

[2] P. R. Rout, T. C. Zhang, P. Bhunia, and R. Y. Surampalli, "Treatment technologies for emerging contaminants in wastewater treatment plants: a review," *Science of the Total Environment*, vol. 753, 2021.

[3] A. Adewuyi, "Chemically modified biosorbents and their role in the removal of emerging pharmaceutical waste in the water system," *Water*, vol. 12, no. 6, p. 1551, 2020.

[4] N. H. Tran and K. Y. H. Gin, "Occurrence and removal of pharmaceuticals, hormones, personal care products, and endocrine disrupters in a full-scale water reclamation plant," *Science of the Total Environment*, vol. 599, pp. 1503–1516, 2017.

[5] M. Bashir, M. Batool, N. Arif, M. Tayyab, Y. J. Zeng, and M. Nadeem Zafar, "Strontium-based nanomaterials for the removal of organic/inorganic contaminants from water: a review," *Coordination Chemistry Reviews*, vol. 492, 2023.

[6] S. F. Ahmed, M. Mofijur, S. Nuzhat et al., "Recent developments in physical, biological, chemical, and hybrid treatment techniques for removing emerging contaminants from wastewater," *Journal of Hazardous Materials*, vol. 416, 2021.

[7] B. S. Rathi, P. S. Kumar, and P. L. Show, "A review on effective removal of emerging contaminants from aquatic systems: current trends and scope for further research," *Journal of Hazardous Materials*, vol. 409, 2021.

[8] J. M. Philip, U. K. Aravind, and C. T. Aravindakumar, "Emerging contaminants in Indian environmental matrices–a review," *Chemosphere*, vol. 190, pp. 307–326, 2018.

[9] B. Díaz-Garduño, M. G. Pintado-Herrera, M. Biel-Maeso et al., "Environmental risk assessment of effluents as a whole emerging contaminant: efficiency of alternative tertiary treatments for wastewater depuration," *Water Research*, vol. 119, pp. 136–149, 2017.

[10] A. Ansari Moghaddam, L. Mohammadi, E. Bazrafshan et al., "Antibiotics sequestration using metal nanoparticles: an updated systematic review and meta-analysis," *Inorganica Chimica Acta*, vol. 550, 2023.

[11] A. Ghamkhari, L. Mohamadi, S. Kazemzadeh, M. N. Zafar, A. Rahdar, and R. Khaksefidi, "Synthesis and characterization of poly (styrene-block-acrylic acid) diblock copolymer modified magnetite nanocomposite for efficient removal of penicillin G," *Composites Part B: Engineering*, vol. 182, 2020.

[12] Z. H. Mussa, F. F. Al-Qaim, A. H. Jawad, M. Scholz, and Z. M. Yaseen, "A comprehensive review for removal of non-steroidal anti-inflammatory drugs attained from wastewater observations using carbon-based anodic oxidation process," *Toxics*, vol. 10, p. 598, 2022.

[13] Y. Praveenkumarreddy, K. Vimalkumar, B. R. Ramaswamy et al., "Assessment of non-steroidal anti-inflammatory drugs from selected wastewater treatment plants of Southwestern India," *Emerging Contaminants*, vol. 7, pp. 43–51, 2021.

[14] A. Rastogi, M. K. Tiwari, and M. M. Ghangrekar, "A review on environmental occurrence, toxicity and microbial degradation of Non-Steroidal Anti-Inflammatory Drugs (NSAIDs)," *Journal of Environmental Management*, vol. 15, no. 300, 2021.

[15] Y. A. J. Al-Hamadani, C. M. Park, L. N. Assi et al., "Sonocatalytic removal of ibuprofen and sulfamethoxazole in the presence of different fly ash sources," *Ultrasonics Sonochemistry*, vol. 39, pp. 354–362, 2017.

[16] J. L. Wu, Z. H. Liu, Q. G. Ma, L. Dai, and Z. Dang, "Occurrence, removal, and risk evaluation of ibuprofen and acetaminophen in municipal wastewater treatment plants: a critical review," *Science of the Total Environment*, vol. 891, 2023.

[17] L. H. Heckmann, R. Connon, H. L. Hooper et al., "Molecular and population stress responses of Daphnia magna exposed to ibuprofen," in *Proceedings of the SETAC Europe 15th Annual Meeting*, pp. 308-309, Lille, France, January 2005.

[18] M. Parolini, "Toxicity of the Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) acetylsalicylic acid, paracetamol, diclofenac, ibuprofen and naproxen towards freshwater invertebrates: a review," *Science of the Total Environment*, vol. 20, no. 740, 2020.

[19] L. H. Santos, A. N. Araújo, A. Fachini, A. Pena, C. Delerue-Matos, and M. C. B. S. M. Montenegro, "Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment," *Journal of Hazardous Materials*, vol. 175, no. 1-3, pp. 45–95, 2010.

[20] J. Jan-Roblero and J. A. Cruz-Maya, "Ibuprofen: toxicology and biodegradation of an emerging contaminant," *Molecules*, vol. 28, no. 5, p. 2097, 2023.

[21] Y. Guo, P. S. Qi, and Y. Z. Liu, "A review on advanced treatment of pharmaceutical wastewater," *IOP Conference Series: Earth and Environmental Science*, vol. 63, p. 012025, 2017.

[22] A. Shraim, A. Diab, A. Alsuhaimi et al., "Analysis of some pharmaceuticals in municipal wastewater of Almadinah Almunawarah," *Arabian Journal of Chemistry*, vol. 10, no. 1, pp. S719–S729, 2017.

[23] G. Pooja, P. S. Kumar, G. Prasannamedha, S. Varjani, and D. V. Vo, "Sustainable approach on removal of toxic metals from electroplating industrial wastewater using dissolved air flotation," *Journal of Environmental Management*, vol. 295, 2021.

[24] Y. J. Liu, S. L. Lo, Y. H. Liou, and C. Y. Hu, "Removal of nonsteroidal anti-inflammatory drugs (NSAIDs) by electrocoagulation-flotation with a cationic surfactant," *Separation and Purification Technology*, vol. 152, pp. 148–154, 2015.

[25] Y. Lu, B. Chen, M. Yu et al., "Simultaneous separation/enrichment and detection of trace ciprofloxacin and lomefloxacin in food samples using thermosensitive smart polymers aqueous two-phase flotation system combined with HPLC," *Food Chemistry*, vol. 210, pp. 1–8, 2016.

[26] M. Choi, D. W. Choi, J. Y. Lee, Y. S. Kim, B. S. Kim, and B. H. Lee, "Removal of pharmaceutical residue in municipal wastewater by DAF (dissolved air flotation)–MBR (membrane bioreactor) and ozone oxidation," *Water Science and Technology*, vol. 66, no. 12, pp. 2546–2555, 2012.

[27] Y. F. Li, T. Fang, Y. C. Lee, Y. J. Liu, C. Y. Hu, and S. L. Lo, "Cationic surfactants influencing the enhancement of energy efficiency for perfluorooctanoic acid (PFOA) removal in the electrocoagulation-flotation (ECF) system," *Chemosphere*, vol. 318, 2023.

[28] L. H. V. Thanh and J. C. Liu, "Ion flotation of palladium by using cationic surfactants – effects of chloride ions," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 616, 2021.

[29] E. N. Yunira, A. Suryani, S. Tursiloadi, and S. Tursiloadi, "Synthesis and aplication CTAC surfactant from palmityl alcohol in insecticide emulsifiable concentrate formulation IOP Conf. Ser: earth and," *IOP Conference Series: Earth and Environmental Science*, vol. 209, p. 012039, 2018.

[30] A. V. Kolesnikov, V. V. Kuznetsov, V. A. Kolesnikov, and Y. I. Kapustin, "The role of surfactants in the electroflotation extraction of copper, nickel, and zinc hydroxides and phosphates," *Theoretical Foundations of Chemical Engineering*, vol. 49, no. 1, pp. 1–9, 2015.

[31] H. Shayesteh, F. Raji, and A. R. Kelishami, "Influence of the alkyl chain length of surfactant on adsorption process: a case study," *Surfaces and Interfaces*, vol. 22, 2021.

[32] S. Aggarwal and S. Ikram, "Chapter 6-Surface modification of polysaccharide nanocrystals," *Innovation in Nano-Polysaccharides for Eco-sustainability*, pp. 133–161, 2022.

[33] Y. F. Li, W. Y. Chien, Y. J. Liu, Y. C. Lee, S. L. Lo, and C. Y. Hu, "Perfluorooctanoic acid (PFOA) removal by flotation with cationic surfactants," *Chemosphere*, vol. 266, 2021.

[34] M. G. Craioveanu, L. Stoica, C. Constantin, and O. Oprea, "Cr (III)aq separation by flotation with multipolar collector," *Separation Science and Technology*, vol. 55, no. 2, pp. 346–357, 2019.

[35] R. Bürger, S. Diehl, M. C. Martí, and Y. Vásquez, "Simulation and control of dissolved air flotation and column froth flotation with simultaneous sedimentation," *Water Science and Technology*, vol. 81, no. 8, pp. 1723–1732, 2020.

[36] A. Srinivasan and T. Veraraghavan, "Dissolved air flotation in industrial wastewater," *Treatment. Water and Wastewater Treatment Technologies*, vol. 1, pp. 111-112, 2011.

[37] F. Capponi, M. Sartori, M. L. Souza, and J. Rubio, "Modified column flotation of adsorbing iron hydroxide colloidal precipitates," *International Journal of Mineral Processing*, vol. 79, no. 3, pp. 167–173, 2006.

[38] J. Drzymala and P. B. Kowalczuk, "Classification of flotation frothers," *Minerals*, vol. 8, no. 2, p. 53, 2018.

[39] A. Tewari, A. Bagchi, A. Raha, P. Mukherjee, and M. Pal, "Preparation, Estimation and Validation of the parameters of

the standard curve of Ibuprofen by comparative study," *Asian Journal of Pharmacy and Pharmacology*, vol. 3, no. 3, pp. 79–85, 2017.

[40] L. Chang, Y. Cao, W. Peng et al., "Insight into the effect of oxidation degree of graphene oxides on their removal from wastewater via froth flotation," *Chemosphere*, vol. 262, 2021.

[41] S. Oh, W. S. Shin, and H. T. Kim, "Effects of pH, dissolved organic matter, and salinity on ibuprofen sorption on sediment," *Environmental Science and Pollution Research*, vol. 23, no. 22, pp. 22882–22889, 2016.

[42] T. X. Bui and H. Choi, "Adsorptive removal of selected pharmaceuticals by mesoporous silica SBA-15," *Journal of Hazardous Materials*, vol. 168, no. 2-3, pp. 602–608, 2009.

[43] S. Rahimi, M. Irannajad, and A. Mehdilo, "Comparative studies of two cationic collectors in the flotation of pyrolusite and calcite," *International Journal of Mineral Processing*, vol. 167, pp. 103–112, 2017.

[44] P. P. Meng, S. B. Deng, A. Maimaiti et al., "Efficient removal of perfluorooctane sulfonate from aqueous film forming foam solution by aeration-foam collection," *Chemosphere*, vol. 203, pp. 263–270, 2018.

[45] K. D. Danov, P. A. Kralchevsky, and K. P. Ananthapadmanabhan, "Micelle-monomer equilibria in solutions of ionic surfactants and in ionic-nonionic mixtures: a generalized phase separation model," *Advances in Colloid and Interface Science*, vol. 206, pp. 17–45, 2014.

[46] H. N. Abd Alhuseen and N. N. Abdulrazzaq, "Flotation of cadmium ions from wastewater using air micro-bubbles," *Journal of Ecological Engineering*, vol. 24, no. 8, pp. 95–105, 2023.

[47] G. Z. Kyzas, N. K. Lazaridis, and K. A. Matis, "Flotation: recent innovations in an interesting and effective separation process," *Interface Science and Technology*, vol. 30, pp. 15–42, 2019.

[48] J. Choi, E. Lee, S. Q. Choi, S. Lee, Y. Han, and H. Kim, "Arsenic removal from contaminated soils for recycling via oil agglomerate flotation," *Chemical Engineering Journal*, vol. 285, pp. 207–217, 2016.

[49] X. Zheng, J. P. Franzidis, N. W. Johnson, and E. V. Manlapig, "Modelling of entrainment in industrial flotation cells: the effect of solids suspension," *Minerals Engineering*, vol. 18, no. 1, pp. 51–58, 2005.

[50] J. C. M. Chapelain, S. Faure, and D. Beneventi, "Clay flotation: effect of TTAB cationic surfactant on foaming and stability of illite clay microaggregates foams," *Industrial & Engineering Chemistry Research*, vol. 55, no. 7, pp. 2191–2201, 2016.

[51] S. Farrokhpay, M. Ostadrahimi, S. Pirmoradi, and M. Noparast, "Effect of air flow rate and froth depth on the flotation performance: an industrial case study in a 10 m^3 cell," *Physicochemical Problems of Mineral Processing*, vol. 58, no. 5, 2022.

[52] S. Schmideder, L. Thurin, G. Kaur, and H. Briesen, "Inline imaging reveals evolution of the size distribution and the concentration of microbubbles in dissolved air flotation," *Water Research*, vol. 224, 2022.

[53] A. B. Said, F. Frances, A. Grandjean, C. Latrille, and S. Faure, "Study of a foam flotation process assisted by cationic surfactant for the separation of soil clay particles: processing parameters and scaling-up sensitivity," *Chemical Engineering and Processing-Process Intensification*, vol. 142, 2019.

[54] A. I Alwared, N. Abdulrazzaq, and B. Al-Sabbagh, "Microbubble flotation for removing cadmium ions from aqueous solution: artificial neural network modeling and kinetic of flotation," *IJCPE*, vol. 20, no. 2, pp. 1–9, 2019.

[55] S. K. Mehta, B. G. Ram, and G. Ram, "Behavior of papain in mixed micelles of anionic–cationic surfactants having similar tails and dissimilar head groups," *Journal of Colloid and Interface Science*, vol. 344, no. 1, pp. 105–111, 2010.

[56] G. Kume, M. Gallotti, and G. Nunes, "Review on anionic/cationic surfactant mixtures," *Journal of Surfactants and Detergents*, vol. 11, pp. 1–11, 2008.

[57] J. Tian, L. H. Xu, W. Deng, H. Jiang, Z. Y. Gao, and Y. H. Hu, "Adsorption mechanism of new mixed anionic/cationic collectors in a spodumene-feldspar flotation system," *Chemical Engineering Science*, vol. 164, pp. 99–107, 2017.

[58] X. Z. Yuan, Y. T. Meng, G. M. Zeng, Y. Y. Fang, and J. G. Shi, "Evaluation of tea-derived biosurfactant on removing heavy metal ions from dilute wastewater by ion flotation," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 317, no. 1-3, pp. 256–261, 2008.

[59] Y. T. Meng, X. Z. Yuan, G. M. Zeng, J. G. Shi, and Y. Y. Fang, "Removal of cadmium from wastewater with plant-derived biosurfactant tea saponin by ion flotation," *Acta Scientiae Circumstantiae*, vol. 25, pp. 1029–1033, 2005.

[60] M. Maniavannan, P. Parthiban, P. Ilayaraja, and J. Rathinavel, "GC-MS validation of the organic ionic impurity tetra-n-butylammonium bromide in Teneligliptin," *Journal of Applied Pharmaceutical Science*, vol. 13, no. 07, pp. 220–225, 2023.

[61] L. P. Cunico, D. S. Damaceno, R. M. Matricarde Falleiro et al., "Vapour liquid equilibria of monocaprylin plus palmitic acid or methyl stearate at P = (1.20 and 2.50) kPa by using DSC technique," *The Journal of Chemical Thermodynamics*, vol. 91, pp. 108–115, 2015.

[62] S. Xu, L. Zou, X. Ling, Y. Wei, and S. Zhang, "Preparation and thermal reliability of methyl palmitate/methyl stearate mixture as a novel composite phase change material," *Energy and Buildings*, vol. 68, pp. 372–375, 2014.

[63] C. Hao, X. Zhao, and P. Yang, "GC-MS and HPLC-MS analysis of bioactive pharmaceuticals and personal-care products in environmental matrices," *TrAC, Trends in Analytical Chemistry*, vol. 26, no. 6, pp. 569–580, 2007.

[64] J. M. Traverso-Soto, E. González-Mazo, and P. A. Lara-Martín, "Analysis of surfactants in environmental samples by chromatographic techniques," *Intech*, vol. 7, 2011.

[65] S. González, M. Petrovic, M. Radetic, P. Jovancic, V. Ilic, and D. Barceló, "Characterization and quantitative analysis of surfactants in textile wastewater by liquid chromatography/quadrupole-time-of-flight mass spectrometry," *Rapid Communications in Mass Spectrometry*, vol. 22, no. 10, pp. 1445–1454, 2008.

[66] X. Bu, G. Xie, Y. Peng, and Y. Chen, "Kinetic modeling and optimization of flotation process in a cyclonic microbubble flotation column using composite central design methodology," *International Journal of Mineral Processing*, vol. 157, pp. 175–183, 2016.

[67] X. Yang, X. Bu, G. Xie, and S. Chehreh Chelgani, "A comparative study on the influence of mono, di, and trivalent cations on the chalcopyrite and pyrite flotation," *Journal of Materials Research and Technology*, vol. 11, pp. 1112–1122, 2021.

[68] X. Bu, G. Xie, Y. Peng, L. Ge, and C. Ni, "Kinetics of flotation. Order of process, rate constant distribution and ultimate recovery," *Physicochemical Problems of Mineral Processing*, vol. 53, pp. 342–365, 2017.

[69] X. Hu, Z. Tong, J. Sha et al., "Effects of flotation reagents on flotation kinetics of aphanitic (microcrystalline) graphite," *Separations*, vol. 9, no. 12, p. 416, 2022.
[70] M. Alvarez-Silva, L. Vinnett, R. Langlois, and K. E. Waters, "A comparison of the predictability of batch flotation kinetic models," *Minerals Engineering*, vol. 99, pp. 142–150, 2016.
[71] L. Chang, Y. Cao, W. Peng et al., "Efficiently removing cetyl trimethyl ammonium bromide from wastewater by graphene oxide," *Surface and Interface Analysis*, vol. 21, p. 9, 2020.
[72] G. Z. Kyzas, A. C. Mitropoulos, and K. A. Matis, "From microbubbles to nanobubbles: effect on flotation," *Processes*, vol. 9, no. 8, p. 1287, 2021.
[73] G. Kyzas and K. A. Matis, "Flotation in water and wastewater treatment," *Processes*, vol. 6, no. 8, p. 116, 2018.